

The Role of the Molecular Association in the Change of the Sign of the Soret Coefficient in Aqueous Mixtures

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The change of sign with composition in aqueous mixtures of associating fluids is analysed by means of Molecular Dynamics simulations. The results obtained are in quantitative agreement with the experimental data in water-ethanol and water-methanol solutions, which exhibit the mentioned change of sign. A subsequent theoretical analysis is addressed to establish a relationship between the dependence of the Soret coefficient with composition with the existence of large inter-species interactions. Although the change of sign of the Soret coefficient with composition is not only due to so-called chemical contribution analysed here, we discuss the role that these interactions play in such a change of sign.

Aqueous solutions often exhibit a non-ideal behaviour in both thermodynamic and in dynamic properties, due to the existence of strong, very directional hydrogen-bond interactions [1, 2]. One of the most astonishing features observed in many aqueous mixtures is the change of the sign of the *thermal diffusion* factor, or Ludwig-Soret coefficient, with composition [3]. This phenomenon has been observed since long time ago but despite many efforts there is not even a qualitative microscopic picture of the effect yet. The work addressed in this letter is twofold: on one hand, we present, to the best of our knowledge, the first molecular dynamics simulations able to quantitatively reproduce the experimental values of the thermal diffusion factor in aqueous solutions of associating fluids, including the change of sign of this coefficient with composition. In the light of these results and MD simulations of mixtures of Lennard-Jones particles of hypothetical compounds, we analyse the role played by strong cross-interactions on the composition dependence of the thermal diffusion coefficient, and its influence on its change of sign.

When a binary mixture is under a thermal gradient, one component will enrich in the cold region while the other will migrate towards the hot boundary. At the stationnary state, the magnitude of the separation is characterised by the thermal diffusion factor

$$\alpha_T \equiv -\frac{T}{x_A(1-x_A)} \frac{\nabla x_A}{\nabla T}, \quad (1)$$

where x_A is the molar fraction of species A . The Soret coefficient, $S_T = \alpha_T/T$ is also commonly used to quantify the amplitude of the separation. The sign of α_T has a very important meaning: it reflects the direction of separation of the components of the mixture when a thermal

gradient is applied. The generally adopted convention is to take component A as the heaviest one. Thus, α_T is positive when the heaviest species (A) enrich at the cold side, *i.e.* ∇x_A and ∇T have opposite sign. In gas mixtures, α_T is proportional to the mass difference between species, is positive, although this depends on the interaction potential [4], and mostly independent of composition. The situation is less simple in dense fluids. In a recent paper, Debuschewitz and Köhler [5] have shown that the Soret coefficient can be splitted into independent contributions: a mass effect, depending on the mass and moment of inertia difference of the species, and a so-called *chemical* effect. The mass effect is found to be independent of composition, while the composition effect comes solely from the chemical part. In benzene-cyclohexane isotopic mixtures, a change of sign was even observed at a given composition. In mixtures of associating fluids, in some ternary polymer solutions [6, 7] and electrolyte solutions [8], α_T strongly depends on composition. Therefore, the composition dependence of the thermal diffusion factor seems to be completely controled by the different molecular interactions between the constituents, which has been referred to as chemical effect.

To analyse this problem in more depth, we have performed molecular dynamics simulations on several mixtures where strong interactions exist. We present studies of water-ethanol and water-methanol mixtures for which experimental data are available. Moreover, we have also investigated water-acetone and water-dimethyl-sulfoxide mixtures, for which we give our predictions. For all studied systems, a strong composition dependence and a change of sign is observed.

Previous applications of MD simulations to the study of thermal diffusion have been mostly devoted to the development of methodologies [9, 10, 11] and to the study of Lennard-Jones like mixtures [12, 13]. There have been only a few attempts to compute the thermal diffusion factor in molecular liquids [14, 15]. Recently, however, the ability of MD simulations in quantitatively reproducing

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thermal diffusion in pentane-*n*-decane mixtures has been confirmed [16].

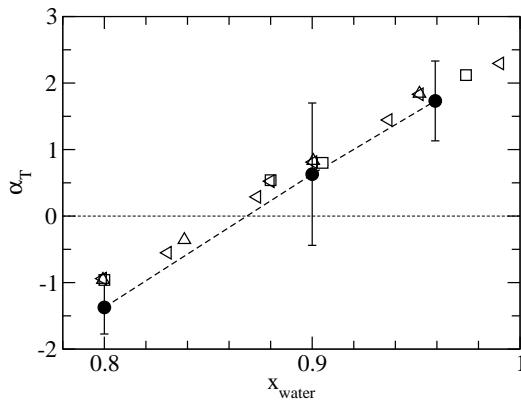


FIG. 1: Thermal diffusion factor versus water molar fraction in water-ethanol mixture at 298 K and 1 atm. Simulation data: ●, experimental data: □ [17], △ [18], ▲ [19]. Dashed line is a guide to the eyes.

In our simulations we have used a non-equilibrium algorithm [20, 21], which permits to maintain a heat flow through the system with control on the average temperature and total momentum and energy conservation. As far as the molecular potentials are concerned, we have chosen simple models able to reproduce strong interactions such as hydrogen bonds. The following force fields were used for self-interactions: for water, the TIP4P model [22]; for methanol and ethanol, the OPLS model of Jorgensen [23]; for acetone, a model proposed by Wheeler and Rowley [24]; and, finally, for DMSO, the force field derived by Luzar and Chandler [25]. Standard Lorentz-Berthelot mixing rules were used for cross interactions. The simulations were carried out on 800 molecules in water-alcohol systems and 500 in the other cases. The details of the simulations will be given elsewhere.

The simulation results for the water-ethanol mixture at ambient conditions are compared with experimental data on fig. 1. It is important to notice that experimental data have been obtained by three different methods [17, 18, 19]. The consistency between experimental results is remarkable and these data can be considered as reference data for this system. As can be seen, our simulation results are in very good agreement with experiments. This validates our methodological choices. A change of sign of α_T is observed for $x_{\text{water}} \approx 0.86$.

In fig. 2, we compare simulation data with experiments for the water-methanol system at 313 K and 1 atm. Experimental data are those of Tichacek *et al.* [26] at the same thermodynamic conditions. We observe a plateau at low water molar fraction followed by a change of sign of α_T at $x_{\text{water}} \approx 0.8$, in agreement with the experimental data. Finally, predictions for the thermal diffusion factor versus water content in water-acetone and water-dimethyl-sulfoxide mixtures are shown in fig. 2. In both cases, a change of sign of α_T is also observed. Therefore,

an important dependence of S_T with composition is observed in these mixtures having strong hydrogen-bonds interactions.

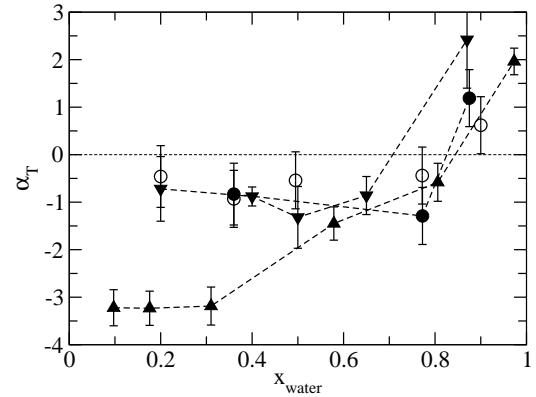


FIG. 2: Thermal diffusion factor versus water molar fraction in water-methanol at 313 K and 1 atm: NEMD data (●) and experiments (○) from Tichacek *et al.* [26]. NEMD data for water-DMSO (▼) and water-acetone (▲) at 298 K and 1 atm. Dashed lines are guide to the eyes.

Despite the ability of MD simulations in reproducing the experimental behaviour, the question about what microscopically causes the strong composition-dependence and, eventually, the change of sign, in α_T remains still open. To shed some light on this question we have built a two-dimensional Ising model in a temperature gradient. In this model, the dynamic process consists of the swap of 2 particles between neighboring sites i and j , kept at different local temperatures T_i and T_j , according to an externally fixed temperature gradient. The presence of species A (or B) on a given lattice site i is represented by the state $\vec{\sigma}_i = (1, 0)$ (or $(0, 1)$) of the local spin. The site-site interactions are limited to first nearest neighbors, and the lattice has no vacancies. The Hamiltonian is given by $H = \sum_{i,j>i} \vec{\sigma}_i \cdot \mathbf{J} \cdot \vec{\sigma}_j$, where \mathbf{J} is a constant square matrix which defines the particle-particle interactions through its elements: ε_{AA} , ε_{BB} , for the intra-species interactions, and $\varepsilon_{AB} = \varepsilon_{BA}$ for the inter-species. The necessary particle number conservation in the process implies a spin-exchange or Kawasaki dynamics [27]. The actual dynamic process is determined through the transition probability for one spin-exchange, which has been chosen to be

$$W([\vec{\sigma}_i, \vec{\sigma}_j] \rightarrow [\vec{\sigma}'_i, \vec{\sigma}'_j]) = \quad (2)$$

$$\min \left[e^{-[(E'_i - E_i)/kT_i + (E'_j - E_j)/kT_j]}, 1 \right]$$

In this expression, E_i is the energy of the spin at the site i , that is

$$E_i = \sum_{k \in (nn)} \vec{\sigma}_i \cdot \mathbf{J} \cdot \vec{\sigma}_k \quad (3)$$

where nn stands for *nearest neighbors*. This transition probability satisfies the required detailed balance condi-

tion so that the appropriate thermodynamic equilibrium is reached if the temperature is uniform.

In fig. 3 we present the results of simulations on the lattice model for different values of ε_{AB} , with $\varepsilon_{AA} = -2.0$ and $\varepsilon_{BB} = -1.0$ in dimensionless units, where $T^* = 2.55$ is the average reduced temperature. The figure clearly

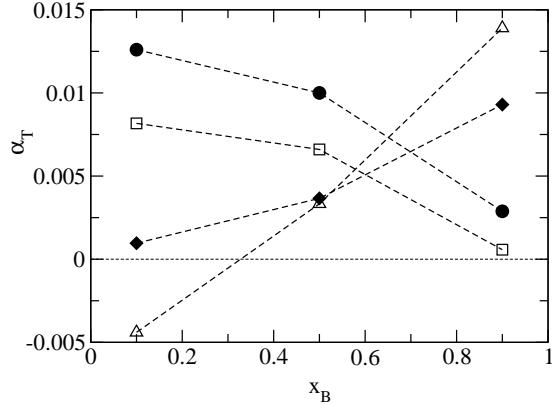


FIG. 3: Thermal diffusion factor α_T for the mixture of particles in function of the molar fraction of one component for several cross interaction parameters $\varepsilon_{AB} = -1.0$ (\bullet), -1.414 (\square), -2.0 (\blacklozenge), -2.546 (\triangle). Dashed lines are guide to the eyes.

shows that the slope of the concentration dependence of α_T changes from positive to negative when ε_{AB} varies from ε_{BB} to ε_{AA} . When $|\varepsilon_{AB}| > |\varepsilon_{AA}|, |\varepsilon_{BB}|$, a change of sign of α_T with composition is in addition observed. This is again a strong suggestion that in dense systems the behaviour of α_T with composition is severely influenced by interactions between unlike species relative to interactions between like species.

Obviously, the lattice model is too simplistic to draw conclusions, but it grasps an important aspect of the phenomenon. It can be therefore interesting to evaluate the role played by the unlike species interactions by doing direct molecular dynamics simulations on a simple Lennard-Jones (LJ) mixture, which corresponds to a more realistic situation. We have thus computed α_T using the same MD methodology as previously described. Both species have the same mass and size ($\sigma = 3.405 \text{ \AA}$), but different energetic parameters ($\varepsilon_{AA} = 0.996$, $\varepsilon_{BB} = 1.384 \text{ kJ mol}^{-1}$). Notice that the values for particle A correspond to argon). For the inter-species energetic parameter, we have used a value of $\varepsilon_{AB} = 2.348 \text{ kJ mol}^{-1}$, much larger than parameters between like species. The thermal energy is $RT = 0.998 \text{ kJ mol}^{-1}$. Simulations have been done in the dense liquid state and care have been taken that no demixion occurred. A change of sign of α_T is again observed. Effectively, for the following compositions, $x_B = 0.1, 0.5, 0.9$, the values of the thermal diffusion are, respectively, $-1.97, -0.187, +1.679$. The fact that systems of Lennard-Jones particles could exhibit a change of sign of α_T with composition has remained unnoticed in previous works, partly because most of studies have made use of the standard Lorentz-Berthelot mixing

rule, which place ε_{AB} between ε_{AA} and ε_{BB} . Obviously, the interesting physics underlying the behaviour of these simple systems under a temperature gradient deserves a deeper analysis and work is in progress.

All these observations therefore suggest that in more realistic systems the chemical potentials at a given space point z are analogous to the energy E_i of a given particle at the i^{th} site in the lattice model, in view of eq. (3). One may thus think the physical system as divided in small mesoscopic slices and the dynamics of matter transfer as being described by a Master equation. In analogy with the Ising model described above, one may argue that the transition probability for an exchange of δn_A moles of A at the slice located at z by $\gamma \delta n_B$ moles of B, initially at the slice $z + \delta$ is proportional to

$$W[z, z + \delta] \propto \frac{e^{-(\mu_A(z) - \gamma \mu_B(z))/kT(z)}}{e^{-(\mu_A(z + \delta) - \gamma \mu_B(z + \delta))/kT(z + \delta)}} \quad (4)$$

The proportionality factor γ is introduced due to the fact that the matter exchange is not necessarily equimolar. We have considered that the variation of volume in the switch of δn_A moles by δn_B should be negligible, so that $\bar{v}_A \delta n_A + \bar{v}_B \delta n_B = 0$ and hence $\gamma = \bar{v}_A / \bar{v}_B$. In eq. (4) δ should be considered as a characteristic microscopic length analogous to the mean free path in kinetic theory of gases. Respectively, μ_A and \bar{v}_A together with μ_B and \bar{v}_B are the local chemical potentials and partial molar volume of species A and B. In steady state, $\partial n_A / \partial t = 0$ and thus a probability balance indicates that

$$\{n_A(z + \delta)W[z + \delta, z] + n_A(z - \delta)W[z - \delta, z] - n_A(z)(W[z, z - \delta] + W[z, z + \delta])\} = 0. \quad (5)$$

Taking δ as a length much smaller than the spatial variation of the thermodynamic fields $T(z)$ and $n_A(z)$, an expansion in powers of δ reveals that, in a system in steady state with no net matter flow, the condition

$$\nabla \left(\frac{\mu_A - \gamma \mu_B}{kT} \right)_P = 0 \quad (6)$$

should be satisfied. In the spirit of Onsager's linear irreversible thermodynamics [28], this result indicates that the effective thermodynamic force causing the whole effect of species separation in a liquid in a temperature gradient is the left hand side of (6). Thus, eq. (6) states that in a system without matter flow, the variation of $(\mu_A - \gamma \mu_B)/kT$ with temperature is compensated by the variation of the same quantity with composition. This point of view permits to obtain a relationship between the temperature gradient and the composition gradient and, therefore, of the thermal diffusion factor, according to eq. (1),

$$\alpha_T = -\frac{\bar{v}_A \bar{v}_B}{x \bar{v}_A + (1 - x) \bar{v}_B} \frac{\bar{h}_A / \bar{v}_A - \bar{h}_B / \bar{v}_B}{x (\partial \mu_A / \partial x)_{P,T}}, \quad (7)$$

where \bar{h}_A and \bar{h}_B are the partial molar enthalpies of the components A and B, respectively. In the derivation, γ

has been taken as constant. Surprisingly, this expression is identical to that proposed by Kempers and very close to that of many authors that have used thermodynamic considerations (see [29] and references therein). The accuracy of this expression has been tested on hydrocarbon mixtures [30], with a reasonable agreement. In associating fluids it is thus expected a change in the sign of the thermal diffusion factor with composition if $\bar{h}_A/\bar{v}_A - \bar{h}_B/\bar{v}_B$ changes sign at some particular point. This change of sign in our picture is caused by large inter-species interactions, larger than the intra-species interactions, which makes the dilute component to be more strongly bound than the concentrated component and then to have a more negative chemical potential. If the molar volumes are the same and, for instance, A is the dilute component, any composition fluctuations will favor A to go downhill in temperature and accumulate preferably on the cold side. This effect is reversed if we vary the concentration up to the point where B is the more dilute component: B is then more strongly bound than A and any composition fluctuations will favor an accumulation of B on the cold side of the box, thus reversing the sign of the Soret coefficient. If the molar volumes are different, any composition fluctuation involves different number of particles of both species present, to maintain the volume constant. Then it is essentially the value of the partial molar enthalpy per unit volume of the components, $\bar{h}_{A,B}/\bar{v}_{A,B}$, which controls the sign of the separation, as it has been already been pointed out in the literature [31].

Equation (6) can be derived maximizing the appropriate Legendre transform of the entropy, the so-called

Massieu-Planck function $S[1/T, P/T]$ [32], locally defined, and subject to the constraint of the constant volume in the composition exchange. This is in fact the approach followed by Kempers. Under these conditions, the separation of the components is purely due to thermodynamic effects, since $(\mu_A - \gamma\mu_B)/k_BT$ is constant along the sample. However, the theory of irreversible processes also considers the existence of a contribution to the thermal diffusion due to purely kinetic origin [28], which is completely ignored in the hypothesis underlying eqs. (2) and (4). An explicit consideration of this kinetic effect would imply the right hand side of eq. (6) to be non-zero. Incorporating such a kinetic effects to the thermodynamic contributions related to the partial molar enthalpies is, to our believe, the main goal of a predictive theory for the Soret effect in describing both, chemical and kinetic effects, in dense systems as well as in dilute gases.

Acknowledgments

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